Allyl Ethers of Carbohydrates. I. Preparation and Polymerization of Tetra-allyl α-Methyl Glucoside

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Results obtained in this Laboratory have shown that allyl ethers of complex carbohydrates such as starch and cellulose form insoluble and infusible resins when exposed to oxygen or air. In an effort to understand more clearly the nature of this insolubilization process, we prepared several allyl derivatives of simpler carbohydrates, and studied the polymerization of these compounds in the presence of air and oxygen at elevated temperatures. Treatment of this kind yielded clear and transparent polymers of the thermosetting type. This paper describes the preparation and polymerization of tetra-allyl α-methyl glucoside.

A few allyl carbohydrates such as α- and β-allyl glucosides,[2] 3-allyl glucose and its osazone,[3] α- and β-allyl galactosides,[4] and allyl cellulose[5] have been prepared. A more detailed investigation of allyl ethers of carbohydrates was made by Tomecko and Adams,[6] who prepared the allyl ethers of α-methyl glucoside, sucrose, inulin, dextrin, starch and cellulose.

Attempts to prepare tetra-allyl α-methyl glucoside following the procedure described by Tomecko and Adams were unsuccessful. Under the conditions of the experiment, the 10% alkali recommended by them hydrolyzed allyl bromide rapidly; at higher concentrations the rate of hydrolysis was reduced considerably. Fifty per cent. alkali proved to be a more satisfactory medium for this reaction.

Since complete substitution of α-methyl glucoside could not be accomplished in one etherification to prepare pure tetra-allyl α-methyl glucoside, it was necessary to treat the nearly completely substituted allyl α-methyl glucoside with sodium and the resulting alcoholate with allyl bromide. The properties of our preparations as compared with those of Tomecko and Adams are shown in Table I.

The table shows the change of properties on transition from incomplete to complete substitution of methyl glucoside. The density, refractive index and specific rotation of the fully substi-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Bourquelot and Bridel, Compt. rend., 155, 437 (1912); Bourquelot, Hérissey and Bridel, ibid., 156, 1493 (1913); Fischer and Strauss, Ber., 45, 2467 (1912); Fischer, Z. physiol. Chem., 108, 3 (1919); Olive, Bull. soc. chim., 13, 254 (1931); Helferich and Cerdeler, Ber., 73B, 532 (1940).

(3) Freudenberg, Hochstetter and Engels, Ber., 58B, 666 (1925).

(4) Bourquelot and Bridel, Compt. rend., 156, 1104 (1913); Pacsu and Ticharich, Ber., 62B, 3008 (1929).

(5) Sakurada, Z. angew. Chem., 42, 549 (1929); Haller and Heckendorn, Helv. Chim. Acta, 24, 85 (1941).

(6) Tomecko and Adams, This Journal, 45, 2698 (1923).

		Allyl α methyl glucoside	Tetra-allyl α-methyl glucoside	Tetra-allyl α-methyl glucoside (Tomecko and Adams)	Calcd. for $C_{16}H_{26}O_6$
Boiling point	°C.	144–145	160–162	182	...
	Mm.	0.15	1.5	1.5	
Density[20]4		1.0505	1.0345	1.1519	...
Refractive index n^{20}_D		1.4748	1.4710	1.4836	...
Specific rotation [α]^{20}D (8% solution in absolute alcohol)		118.6°	115.6°	116.5°	...
Molecular refraction		94.94	95.76	88.18	95.73
Carbon, %		62.34	63.92	64.13	64.38
Hydrogen, %		8.53	8.11	7.93	8.53
Free hydroxyl, %		2.28	<0.1	...	0
Allyl, %		42.8	45.95	...	46.4

tuted compound have lower values; the molecular refraction and analytical data are nearer the theoretical figures for the tetra-allyl compound. On the basis of insufficient analytical data, it is difficult to pass judgment on the purity of the Tomecko and Adams compound. The description of their product as a thick oil suggests, however, that it might have been partly oxidized.

Under the influence of oxygen and heat, the allylated glucoside gradually polymerizes, first to a viscous liquid and finally to a colorless transparent resin. The changes in viscosity occurring during the polymerization of tetra-allyl α-methyl glucoside are shown in Table II. The gradual increase in viscosity, followed by a marked increase to the point of gelation, along with the insoluble and infusible nature of the final product, is characteristic of the formation of a three di-

Table II

POLYMERIZATION OF TETRA-ALLYL α-METHYL GLUCOSIDE AT 97°[a]

Time, minutes	Viscosity, seconds	Viscosity, centistokes
0	2.8	2.7
60	3.2	3.0
120	8.5	8.0
146	17.7	16.8
160	27.8	26.4
182	67.8	64.4
189	93.6	88.6
196	133.6	126.5
204	231.9	219.5
208	∞[b]	∞[b]

[a] The reaction was conducted and the viscosity measured in a modified Ostwald pipet through which oxygen was passed at a uniform rate. [b] During this measurement the material gelled in the tube. A control experiment in an atmosphere of carbon dioxide remained unchanged.
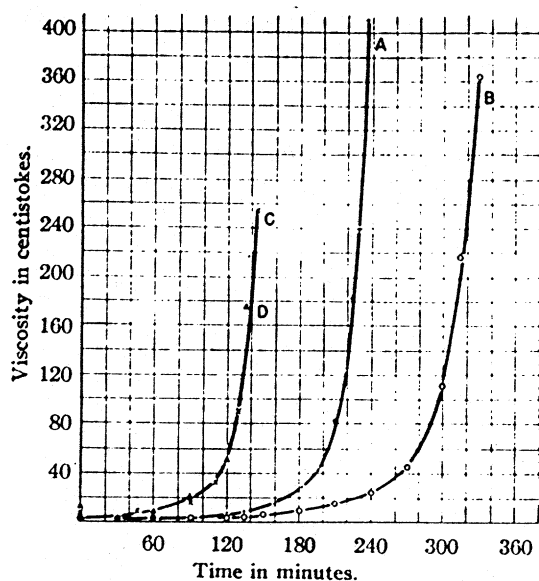
Fig. 1.—Polymerization of allyl methyl glucoside (3.5 allyl groups): A, ●, at 97°, oxygen 26 l. per hour; B, O, at 97°, oxygen 7.5 l. per hour; C, X, at 97°, oxygen 7.5 l. per hr. + Co naphthenate; D, Δ, at 116.5°, oxygen, 7.5 l. per hour.

mensional network.[7] Figure 1 shows the change in viscosity for allyl α-methyl glucoside (with an allyl content corresponding to 3.5 allyl groups per glucoside molecule) under various conditions. Curves A and B show the influence of the rate of flow of oxygen. Curves D and C show the influence of temperature and the addition of a catalyst on the polymerization of the glucoside. The gelation points for these curves are: A, 270 min., B, 390 min., C, 185 min., D, 170 min.

As compared with oxygen, benzoyl peroxide, an efficient catalyst for the vinyl type of polymerization, is relatively ineffective with allyl α-methyl glucoside. To test the effect of benzoyl peroxide two 10-g. portions of allyl α-methyl glucoside (with an allyl content corresponding to 3.5 allyl groups per glucoside molecule) were mixed with 0.1- and 0.2-g. portions of benzoyl peroxide, respectively. The two samples and a control were heated at 100° for sixteen hours. The viscosities (in centistokes) at 25° were 113 for the control, 163 for the sample containing 1% benzoyl peroxide, and 257 for the sample containing 2% benzoyl peroxide. Another sample of the same allyl α-methyl glucoside containing 1% benzoyl peroxide when heated at 180° for ninety-six hours remained fluid and solvent-soluble, although it darkened and the viscosity increased.

Failure of benzoyl peroxide to polymerize completely allyl α-methyl glucoside is apparently due to the fact that an appreciable amount of oxygen is required for this process. The actual amount of oxygen combined was measured in the follow-

(7) Carothers, Trans. Faraday Soc., 32, 39 (1936); Flory, This JOURNAL, 63, 3083, 3091, 3096 (1941).

ing manner: A sample of pure tetra-allyl α-methyl glucoside was heated at 97° while a constant stream of oxygen was passed through it. After three and one-half hours, analysis showed 59.9% carbon and 7.5% hydrogen; after five and one-half hours (which is past the gelation point) the composition was 58.5% carbon and 7.2% hydrogen. Taking into consideration that the formula for tetra-allyl α-methyl glucoside is $C_{19}H_{30}O_6$ (mol. wt. 354.43), it is possible to calculate the number of oxygen atoms (x) combined during the oxidation from the equation[8]

$$x = \frac{12.01 \cdot 19 \cdot 100 - 354.43 \cdot C}{16 \cdot C}$$

where C is the carbon percentage at any given time during the polymerization. Substituting the above carbon values gives 1.7 oxygen atoms for three and one-half hours and 2.2 for five and one-half hours.

At present the manner in which the oxygen is combined in the gelled material is not quite clear. Tests during polymerization showed the presence of peroxides.

Experimental

Preparation of Allyl α-Methyl Glucoside.—500 grams of α-methyl glucoside (m. p. 165–166°, uncor.) was suspended in 890 cc. of allyl bromide in a 5-liter 3-neck flask equipped with condenser, dropping funnel and stirrer. The reaction mixture was maintained at the reflux temperature of allyl bromide (70–75°); 790 cc. of 52% sodium hydroxide was added to the well-stirred reaction mixture dropwise over a period of three and one-half hours. The reaction was allowed to proceed for an additional one and one-half hours. Unreacted allyl bromide and by-products of the reaction, such as allyl ether and allyl alcohol, were removed by steam distillation after the addition of approximately 1.5 liters of water. The oily layer was extracted with two 300-cc. portions of ether. The ether layer was dried with anhydrous sodium sulfate. Distillation from an ordinary Claisen flask in an atmosphere of carbon dioxide yielded from 500 to 540 g. (55–59.0% of theoretical) of a main fraction (I) boiling at 155–160° at 1 mm. This was redistilled through a Vigreux fractionating column fitted with a Whitmore and Lux type still head.[9] The main fraction (II) boiled at 144–145° at 0.14 mm. of mercury. Yields ranged from 403 to 428 g. (44 to 47% of theoretical).

Further Allylation of Allyl α-Methyl Glucoside.—150 grams of fraction II was placed in a 250-cc. flask equipped with a condenser, dropping funnel and glass stirrer; 12.7 g. of metallic sodium was added, and for five hours the reaction mixture was heated between 105 and 110° while it was stirred sufficiently to form small droplets of molten sodium. The temperature of the reaction mixture was then lowered to 80–85°, and 46 cc. of allyl bromide was added slowly dropwise. This reaction mixture was heated for an additional two hours. Sufficient ethanol was added to insure the complete removal of free sodium, and the contents of the flasks were poured into 250 cc. of water; 200 cc. of ether was used to extract allyl glucoside, and the ether layer was washed free of alkali and dried with anhydrous sodium sulfate. After ether was removed at atmospheric pressure, the allyl glucoside was distilled in

(8) This equation is strictly correct only if no losses of volatile material occur during the polymerization. Actual experiments have shown that there is approximately 1 per cent. loss which, on the assumption that the material lost contained 50 per cent. carbon, would give a correction in the second decimal place for x.

(9) Whitmore and Lux, This JOURNAL, 54, 3448 (1932).

vacuo from a Claisen flask, carbon dioxide instead of air being bubbled through the flask. After a small forerun, which was discarded, 142.0 g. of pure tetra-allyl α-methyl glucoside distilled.

Unsaturation in allyl derivatives was determined by the Wijs method. Wijs solution was prepared as recommended by Kemp and Mueller.[10]

Free hydroxyl was determined by acetylating with pyridine-acetic anhydride (3:1) mixture and titrating the uncombined acetyl by a method to be published shortly by W. L. Porter, C. L. Ogg and C. O. Willits of this Laboratory.

(10) Kemp and Mueller, *Ind. Eng. Chem., Anal. Ed.*, 6, 52 (1934).

Summary

The preparation and properties of tetra-allyl α-methyl glucoside are described. Polymerization of this compound in the presence of oxygen is discussed.